Supramolecular Materials

Design and Fabrication of a Flexible and Self-Supporting Supramolecular Film by Hierarchical Control of the Interaction between Hydrogen-Bonded Sheet Assemblies**

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Structural hierarchy is found in highly ordered protein structures and other biological systems, which offer excellent examples for the design and construction of macroscale supramolecular structures by self-assembly through formation of noncovalent bonds.[1] Relatively strong, directional intermolecular interactions, such as hydrogen bonding and

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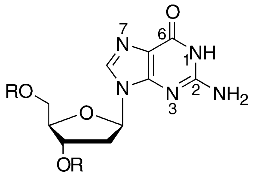
[**] This work was partly supported by a Grant-in-Aid for Scientific Research (grant nos. 14045211 and 14350482) from the Ministry of Education, Science, Sports, and Culture, Japan.

DOI: 10.1002/ange.200352641

coordination, have been effectively used for the construction of well-defined nanometer-scale or mesoscopic assemblies on the molecular level, and various patterns of nanoassemblies have been reported.[2] However, the self-association and self-organization of nanoassemblies into macroscale organized structures are not yet clearly understood since various thermodynamic and kinetic contributions are intricately intertwined in these processes. Therefore, the design and fabrication of materials as macroscale fibers[3] or films,[4] and in other three-dimensional shapes[2,5] with well-defined supramolecular structures are challenging targets and have been attracting much attention. Though supramolecular films can be assembled by stacking mesoscopic two-dimensional sheet assemblies, only a limited number of reports have appeared so far that relate to self-supporting and flexible films.[6] Herein, we report the fabrication of a self-supporting and flexible supramolecular film with a well-defined structural hierarchy through the design of alkylsilylated guanosine derivatives with appropriate molecular structures. Hierarchical control of the stacking of the mesoscopic sheetlike assemblies formed by multiple hydrogen bonds was achieved by tuning the interaction between the sheet assemblies.

In our efforts to develop artificial nucleoside-based supramolecular materials, we found that alkylsilylated guanosine derivative **1** (Scheme 1) showed excellent gelation with alkanes through the formation of a unique sheetlike assembly[7] in which different hydrogen bonds operate on different hierarchical levels. Double interbase hydrogen bonds from 2-NH_2 to 6-C=O and 1-NH to 7-N lead to the formation of a one-dimensional tape motif (Figure 1 a) commonly found for guanosine derivatives.[3c,8] Additional double hydrogen bonds between 2-NH_2 and 3-N connect these tapes to form the two-dimensional sheetlike assembly (Figure 1 b). The intertape hydrogen bonds were cleaved selectively on heating, with a concomitant gel-to-liquid-crystal phase transition. The one-dimensional tape motif formed by the intratape hydrogen bonds was preserved in the liquid-crystal state, which confirms the hierarchy of the intra- and intertape hydrogen bonds. Hierarchical control of the two-dimensional sheet assembly was thus achieved. Our next target was to construct a three-dimensional macroscale structure from the two-dimensional sheets by tuning the intersheet interactions. For this purpose we introduced oxyethylene groups at the ends of the alkylsilyl moieties to give guanosine derivative **2**. This molecular design was expected to result in situation of the oxyethylene groups at the sheet surface and an increase in the intersheet interaction.



1: R=Si(iPr)$_2$C$_8$H$_{17}$
2: R=Si(iPr)$_2$C$_3$H$_6$OC$_2$H$_4$OCH$_3$
3: R=Si(iPr)$_3$
4: R=Si Ph$_2$ tBu

Scheme 1. Chemical structures of trialkylsilyl guanosine derivatives.

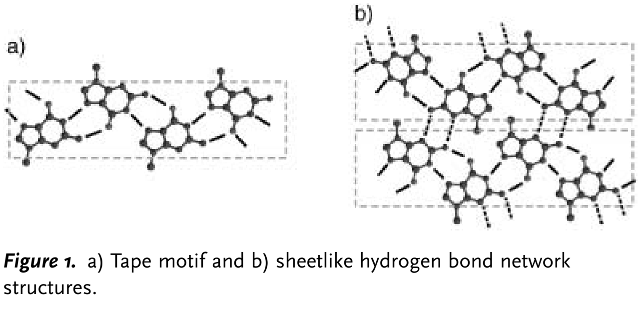


Figure 1. a) Tape motif and b) sheetlike hydrogen bond network structures.

Unlike **1**, nucleoside derivative **2** showed no ability to gelate with alkanes or other common solvents. However, the formation of a flexible translucent film was observed at an air–water interface when dimethylformamide (DMF)/water (1:19 (v/v)) was used as a solvent in the gelation test. Translucent films 0.02–0.10-mm thick were also obtained by casting methanol, ethyl acetate, chloroform, and benzene solutions of **2** (5 % (wt/wt)) onto a flat and smooth teflon plate, with subsequent air-drying and removal from the teflon plate. Unlike Langmuir–Blodgett (LB) films or other films made from low-molecular-weight compounds, the films obtained by this method retained their shape without any support. The spectral and thermal properties of films prepared from different solvents were nearly identical. A similar translucent film was formed by casting onto a glass plate instead of the teflon plate, but it could not be removed from the glass surface. An attempt to fabricate a self-supporting film of **1** by the same procedure was unsuccessful and produced a waxy solid after complete evaporation of the solvent.

The tensile strength of the self-supporting films was 0.51 ± 0.03 MPa, with an average elongation at break of 2.1 ± 0.4 % (20 samples). Although this tensile strength is smaller than that of common polymer films, the obtained films were sufficiently stable and flexible to allow bending (Figure 2). No crystallization was observed with time except when acetone was used as the cast solvent, and the films retained their flexible nature for at least six months at room temperature. No weight loss was observed by thermogravimetry differential thermal analysis below its decomposition temperature (> 200 °C), which shows that solvent molecules are not incorporated in the films. Solvent peaks were not observed

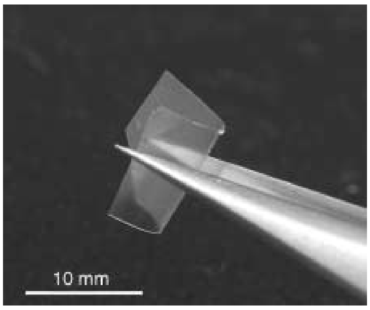


Figure 2. The self-supporting film of **2** produced from an ethyl acetate solution (5 % wt/wt). The film thickness was about 0.03 mm.

in the IR and ^{1}H NMR spectra of the films, which confirms the absence of solvent molecules within the structures.

Figure 3 shows differential scanning calorimetry (DSC) curves of a cast film. The first heating curve of the film (Figure 3a) shows an endothermic peak at 115 °C, at which temperature the film became turbid and fragile. The sharp endothermic peak observed at 130 °C is the melting point of the film, and the sample became a colorless isotropic liquid at this temperature. These peaks were not clearly separated in the second heating curve, and only a broad melting peak was observed at 110–120 °C after repeated heating/cooling cycles (Figure 3c).

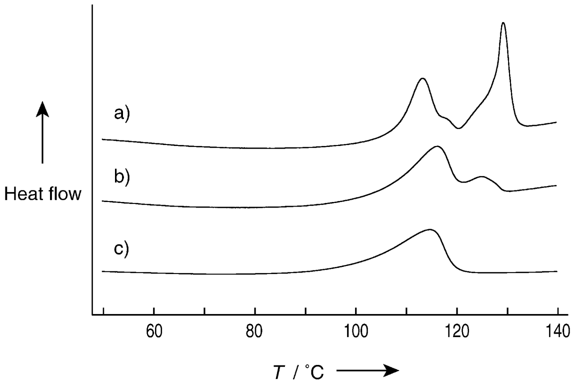


Figure 3. DSC curves of the cast film of **2** upon heating for a) the first, b) the second, and c) the fourth time.

The hydrogen-bonding pattern in the cast film was studied by temperature-controlled IR spectrometry. Crystals of **3** and **4**, whose structures were established by X-ray crystallography,[7] were used as the reference samples and have sheetlike two-dimensional (Figure 1b) and tapelike one-dimensional (Figure 1a) hydrogen bonding network structures, respectively. The spectrum of the film at room temperature (Figure 4b) was similar to that of **3**, with the 2-NH$_2$ deformation peak at 1648 cm^{-1} and no free-NH stretching peak at 3495 cm^{-1}. This observation indicates that the two-dimensional hydrogen-bonding network was the dominant structure in the film. Therefore, introduction of the oxyethylene units had little effect on the hydrogen-bonding pattern of the guanine moieties, and the hydrogen-bonded sheet assemblies were preserved in the cast film of **2**. A shift of the 2-NH$_2$ deformation peak from 1648 to 1630 cm^{-1} and a slight increase in the free-NH stretching peak at 3495 cm^{-1} were observed at around 110 °C (Figure 4c). These peaks are characteristic of the spectrum of **4** (Figure 4d), which suggests that selective cleavage of the intertape hydrogen bonds had occurred to some extent. This temperature corresponds to the first endothermic peak in the first DSC heating curve (Figure 3a). A similar endothermic peak was also observed at the temperature resulting in selective cleavage of the intertape hydrogen bonds for the **1**/dodecane system.[7]

Figure 5 shows the X-ray diffraction pattern of the cast film seen when the incident beam is parallel to the film surface. Fanlike diffraction was observed in the directions normal to the film surface (Figure 5b), which indicates the presence of a lamella-like structure aligned parallel to the film surface. A peak appeared at $2\theta = 4.45°$ ($d = 1.98$ nm), and no additional peak was observed in the smaller-angle range ($0.1° < 2\theta < 4.45°$). The thickness of the hydrogen-bonded sheet in the **1**/dodecane gel was measured by AFM to be 2.5 nm,[7] which corresponds to the sheet assembly with fully extended alkyl chains. In the case of the cast film of **2**, stronger intersheet interaction caused stacking of the sheets. Therefore, the alkylsilyl moieties at the sheet surface might be partially interdigitated with those of the adjacent sheets and/or highly tilted.

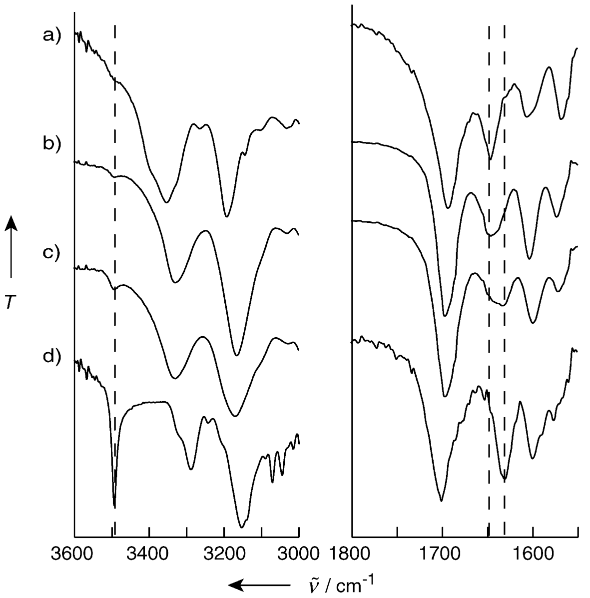


Figure 4. IR spectra of the cast film of **2** and two reference compounds. a) reference compound **3**; b) the cast film of **2** at room temperature; c) the cast film of **2** at 120 °C; d) reference compound **4**. The dashed lines highlight 3495, 1650, and 1629 cm^{-1}.

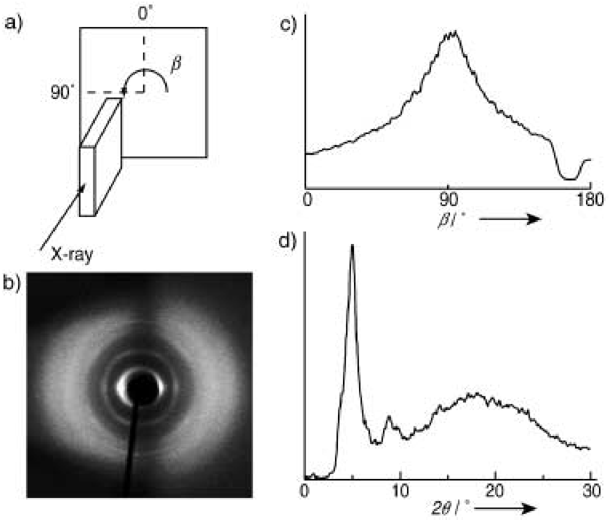


Figure 5. X-Ray diffraction pattern of the cast film of **2**. a) Schematic view of the sample set-up. b) Diffraction pattern collected at the imaging plate. The diffraction profiles along c) the β direction at $2\theta = 4.5$–5.5° and d) the 2θ direction at $\beta = 90°$ are shown.

The well-defined hierarchical structure in the supramolecular film of **2** was thus established. The one-dimensional tape motifs formed by interbase double hydrogen bonds are connected by double intertape hydrogen bonds to form two-dimensional sheet assemblies, and polar intersheet interaction allows fabrication of the flexible, self-supporting film.

Intersheet interaction between the nonpolar surfaces is likely to be limited to van der Waals interaction since the sheet assembly of **1** has its alkyl end groups at the sheet surface. The weak intersheet interaction allowed the penetration of solvent molecules between these sheets and the assembly showed excellent gelation with alkanes (Figure 6a).

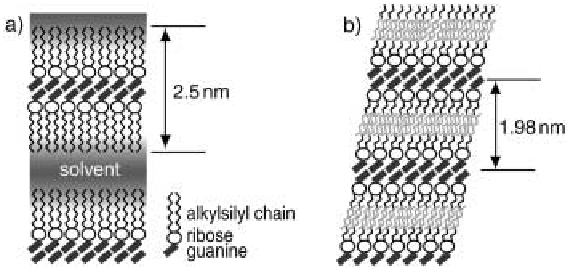


Figure 6. Schematic representation of a) the **1**/alkane gel and b) the cast film of **2**.

However, the intersheet interaction was not strong enough for the fabrication of a self-supporting film and only a waxy solid was produced. In the case of **2** (Figure 6b), stronger intersheet interaction resulted from the introduction of the polar oxyethylene groups at the sheet surface and contributed to the stacking of the sheets to form a lamella-like structure. Thus, a flexible, self-supporting film was obtained. Solvent molecules could no longer penetrate into the space between these sheets and **2** had no gelation ability. The introduction of the polar oxyethylene units had little effect on the hydrogen-bonded sheet assembly, which establishes the hierarchical structure of the film.

The hierarchical control of the interaction between well-defined nanometer-scale and mesoscopic assemblies can cause drastic changes in macroscale shape and properties and allows fabrication of a flexible and self-supporting film. This approach is therefore a promising example of the design and fabrication of supramolecular materials.

Experimental Section

2 was prepared according to the procedure reported previously for similar compounds.[9] 4,7-Dioxaoct-1-ene[9a] (8.12 g, 70 mmol) and a small amount of H_2PtCl_6 (<1 mg) was heated to 100 °C in an N_2 atmosphere. Chlorodiisopropylsilane (10 mL, 59 mmol) was added dropwise and the mixture stirred overnight. After cooling the mixture, the products with low-boiling points were removed (75 Torr, 80 °C) and the residue (6.12 g) was used without further purification. 2′-Deoxyguanosine (1.22 g, 4.6 mmol), imidazole (3.12 g, 45 mmol), and DMF (4.6 mL) were added and the mixture was stirred overnight (N_2, RT). A chloroform solution of the mixture was washed three times with water and purified by column chromatography (Merck silica gel 60, ethanol/chloroform (1:30 v/v)) to give **2** as a white solid (1.08 g, 1.5 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, tetramethylsilane): $\delta = 0.64$ (m, 4H), 0.9–1.2 (m, 28H), 1.68 (m, 4H), 2.38 (m, 1H), 2.56 (m, 1H), 3.3–3.7 (m, 18H), 3.80 (d, 2H), 4.01 (s, 1H), 4.65 (s, 1H), 6.24 (t, 1H), 6.31 (brs, 2H), 7.75 (s, 1H), 12.02 ppm (brs, 1H); elemental analysis: calcd for $C_{34}H_{65}N_5O_8Si_2$: C 56.09, H 9.00, N 9.62 %; found: C 55.95, H 8.72, N 9.94 %; HRMS (FAB): calcd for $C_{34}H_{66}N_5O_8Si_2$ $[M-H]^+$: 728.4449; found: 728.4436.

The ^{1}H NMR spectrum was recorded on a JEOL AL400 spectrometer operating at 400 MHz. The thermal properties were measured on a Rigaku TG8120 or a Perkin-Elmer Pyris 1 DSC instrument. A JEOL WINSPEC100 instrument with an IR-MAU300 infrared microscopy unit and a Mettler FP-800 thermosystem was used for temperature-controlled IR measurements. IP images of X-ray diffraction patterns were obtained with a MAC Science DIP Labo imaging-plate system. Small-angle X-ray scattering data were collected with a Rigaku RINT2500V diffractometer in the range $0.1° < 2\theta < 10°$. The tensile strength of the film was measured by a Tensilon model UTM-II instrument (Toyo Keisoku Kiki Co.) with a cross-head speed of 0.4 mm min^{-1}.

Received: August 13, 2003 [Z52641]

Keywords: hydrogen bonds · nucleosides · self-assembly · supramolecular chemistry · thin films

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